2-Nitroethanol.—This material was purchased from Columbia Organic Chemicals, Columbia, S. C.

2-Nitroethyl Acetate.—The acetate was prepared by sulfuric acid-catalyzed esterification with acetic anhydride.[10a,b] The ester boiled at 68–69° (1.2 mm.) [lit.,[10b] b.p. 62–64° (1.3 mm.)]; yield, 83–85%. The compound possessed $\lambda\lambda_{\max}^{\text{film}}$ 5.72 (carbonyl), 6.40 and 6.92 (nitro), and 8.10 (acetate).

1,2,3,4,5,6,7,8,9,10,11,14-Dodecahydro-9-nitrophanenthrene (*1*).—In a typical preparation, 2-nitroethyl acetate (19.6 g., 0.148 mole) was added dropwise over a 30-min. period to a stirred suspension of sodium acetate (12.4 g., 0.150 mole) and a solution of bi-1-cyclohexen-1-yl (24.0 g., 0.148 mole) in benzene (155 ml.). Afterwards, the two-phase mixture was refluxed for 16 hr.; previous model experiments had shown that a maximum yield was obtained at the end of this period. The cooled reaction mixture was filtered through a sintered funnel and the inorganic salts were washed with hot benzene (2 × 10 ml.). The combined organic phases were treated with Norit, were refiltered, and were evaporated to dryness *in vacuo* to leave a red oil. This material was twice crystallized from alcohol and then was sublimed readily at 60° (0.1 mm.); yield, 14.2 g. (40.9%); m.p. 72.5–73.4° (lit.,[1] m.p. 74.0–74.8°); the solid produced a single peak on gas phase chromatography using a 20% SE-30 on an acid-washed Chromosorb P column at 178°; thin-layer chromatography showed a single spot near the solvent front with pentane as the eluent. The nitro olefin exhibited no selective absorption in the ultraviolet above 210 mμ; $\lambda\lambda_{\max}$ 3.41 and 3.51 (aliphatic olefin), 6.52 and 7.25 (nitro), and 12.95 (ring methylene). The n.m.r. spectrum contained signals centered at 4.60 (the hydrogen attached to the carbon holding the nitro group), 2.80 and 2.60 (integrated area equivalent to one and two hydrogens, respectively), and a series of overlapping peaks stretching from 1.98 to 1.47 (miscellaneous aliphatic hydrogens).

Anal. Calcd. for $C_{14}H_{21}NO_2$: C, 71.45; H, 9.00; N, 5.95. Found: C, 71.48; H, 9.15; N, 5.73.

1,2,3,4,5,6,7,8,9,10,11,12-Dodecahydro-9-ketophenanthrene (*3*).—A cold solution of sodium hydroxide (5.00 g., 0.125 mole) in ethanol (100 ml.) was slowly added to a chilled stirred solution of nitro olefin *1* (10.9 g., 0.0424 mole) in ethanol (100 ml.). The combined liquids were held at 0–2° under a nitrogen atmosphere for 30 min. and were then poured into a cold, dilute hydrochloric acid solution (2 *N*, 300 ml.). The resulting mixture was stirred at 5° for 2 hr. and was allowed to warm to room temperature over a day. The organic material was extracted with ether (3 × 300 ml.) and the combined extracts were dried over magnesium sulfate and were taken to dryness *in vacuo* to leave a brown oil, wt. 9.5 g. Thin-layer chromatography with benzene as the eluent revealed the presence of four components. The infrared spectrum exhibited two carbonyl bands—5.85 (β,γ-ketone *2*) and 6.01 (α,β-ketone *3*); some starting material was noted, also (6.49 and 7.25). Gas phase chromatography using a silicone rubber on an acid-washed Firebrick column at 150° produced four separable peaks: unknown material, β,γ-ketone *2*, α,β-ketone *3*, and nitro olefin *1*. It was not possible to separate the two ketones by column chromatography with silicic acid and petroleum ether.

An effort to distil the ketone mixture revealed that the application of heat was isomerizing compound *2* into the desired *3*; therefore, the impure brown oil (1.0 g.) was distilled slowly at 70° (0.12 mm.) to yield a pale yellow oil (0.46 g.). This latter product gave a major peak (95%) and a minor, trailing peak (5%) on gas phase chromatography using a 20% SE-30 on an acid-washed Chromosorb P column at 202°; thin-layer chromatography showed a single spot with benzene as the eluent; $\lambda_{\max}$ 248 (log ϵ 4.09); $\lambda\lambda_{\max}^{\text{film}}$ 6.03 (carbonyl) and 6.19 (double bond); and $n^{23}\text{D}$ 1.5472. The n.m.r. spectrum did not contain any olefinic proton absorptions. The physical constants of *3* were not further improved by preparative gas chromatography.

Anal. Calcd. for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 81.10; H, 9.82.

The brilliant red 2,4-dinitrophenylhydrazone was crystallized from ethyl acetate–grain alcohol (1:1) and then from ethanol; m.p. 231.0–231.5° (lit.,[1] 233.5–234.1°); $\lambda\lambda_{\max}^{\text{CHCl}_3}$ 258 (log ϵ 4.25), 290 (shoulder) (log ϵ 3.42), and 393 (log ϵ 4.46 [lit.,[1] $\lambda\lambda_{\max}^{\text{CHCl}_3}$ 260 (log ϵ 4.31) and 293 (inflection)].

Anal. Calcd. for $C_{20}H_{24}N_4O_4$: C, 62.48; H, 6.29; N, 14.58. Found: C, 62.46; H, 6.36; N, 14.58.

The white semicarbazone was crystallized from methanol-ether (1:1), m.p. 181.5–182.0°; $\lambda_{\max}^{\text{CH}_3\text{OH}}$ 268 (log ϵ 4.52).

Anal. Calcd. for $C_{15}H_{23}N_3O$: C, 68.93; H, 8.87; N, 16.08. Found: C, 68.66; H, 9.05; N, 15.80.

Acid Hydrolysis of 1,2,3,4,5,6,7,8,9,10,11,14-Dodecahydro-9-nitrophenanthrene.—The nitro olefin *1* (0.253 g., 0.0011 mole) was refluxed with grain alcohol (100 ml.) containing concentrated hydrochloric acid (0.20 ml.) for 15 days. The solvent was removed *in vacuo* to afford a brown oil which was analyzed by gas chromatography using a 5% SE-30 on an acid-washed Chromosorb W column at 212°. The composition of the crude product was as follows (arranged in order of increasing retention time): other products (4%), β,γ-ketone (30%), α,β-ketone (25%), and starting material (41%).

A second reaction involved nitro olefin (0.520 g., 0.0022 mole) and a mixture of ethanol (80 ml.) and dilute hydrochloric acid (1 *N*, 170 ml.) which was boiled for 12 days. Work-up of the crude oil produced a similar result: unknown materials (8%), β,γ-ketone (41%), α,β-ketone (33%), and starting compound (18%).

Finally, nitro olefin (0.520 g.) was heated with dilute hydrochloric acid (1 *N*, 250 ml.) for 15 days. The oil (0.283 g.) was comprised of other compounds (5%), β,γ-ketone (40%), α,β-ketone (35%), and nitro olefin (20%).

Acknowledgment.—The authors are indebted to Mrs. Dalia Aguilar for the infrared and ultraviolet absorption spectra, to Dr. Lois J. Durham for discussions concerning the n.m.r. data, and to Mr. Erich H. Meier for the microanalyses.

The Synthesis of (+)-3-Methyl-β-citronellal

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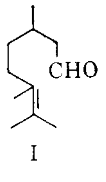
The synthesis of DL-3-methyl-β-citronellal (DL-V) has been accomplished[1] by the selective hydrogen-



I

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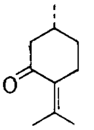
[10] (a) R. B. Kaplan and H. Shechter, *J. Org. Chem.*, **26**, 982 (1961), footnote 11a. (b) H. L. Cates, Jr., Ph.D. thesis, The Ohio State University, 1951, p. 106.

[1] Y. R. Naves, *Bull. soc. chim. France*, 519 (1952).

ation of 3-methyl-β-citral (I). The preparation of optically active V or any other active 3-alkyl or aralkyl substituted β-citronellals has not as yet been reported. Since these compounds have potential use as aroma and vitamin intermediates we wish to report a three-step synthesis of (+)-3-methyl-β-citronellal[2] (V) by a synthetic route that is useful for preparing other 3-alkyl or aralkyl derivatives.

The sodium *t*-amylate-catalyzed methylation of (+)-pulegone (II) by the procedure of Conia[3] gave a 71.5% yield of methylisopulegone fraction. The ultraviolet spectrum of this material gave a maximum at 254 mμ indicating the presence of pulegone or possibly a 2-methylated pulegone isomer.[4] A gas liquid chromatograph (GLC), revealed three components, A (12.3%), B (51.4%), and C (36.3%), in order of elution.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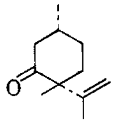
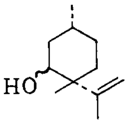
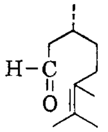

III

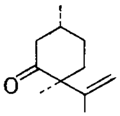

IV


V

Component C was identified as unchanged pulegone by matching its GLC retention time with authentic pulegone. Evidence that II was the only system causing the 254-mμ absorption in these fractions was established by the comparison of % pulegone calculated from GLC (36.3%) with that obtained from ultraviolet data (37.5%). The good agreement of these values rules out any more than trace amounts of a 2-methylisopulegone[4] isomer.

The major constituent B was shown to be the desired (−)-4-methylisopulegone (III) by matching its retention time with a pure sample obtained through the semicarbazone separation procedure of Conia.[3a]

The first component A was thought to be isopulegone[5] on the basis of its elution time in reference to pulegone and on the observation of Conia[3a] that when pulegone was treated for a few minutes with sodium *t*-amylate[5] the recovered "pulegone" had a lower ultraviolet absorption, presumably due to the presence of isopulegone. However, comparison with a known sample proved this to be incorrect. Since the presence of 2-methylated pulegone has been ruled out it is assumed that A is the other 4-methyl isomer IIIa. Recent work by Djerassi[6] and co-workers lend additional support to the assignment of A as IIIa since they report that the base catalyzed methylation of pulegone gave an 83:17 ratio of III and IIIa while in the present work an 81:19 ratio was obtained.


IIIa

The lithium aluminum hydride reduction of pure III gave 4-methylisopulegol (IV) that was shown by GLC to be 43:57 mixture of two isomers. Since axial alcohols are known[7] to be eluted earlier than their equatorial isomers in chromatographic separations our earlier eluted isomer (43%) is presumably the axial alcohol while the other isomer (57%) contains an equatorial hydroxyl group.

The pyrolysis of isopulegol has been reported by Grignard[8] and Doeuvre to give a good yield of β-citronellal. Using a modification of their procedure we pyrolyzed IV at 500° in an inert atmosphere. The resultant pyrolysate was treated with isobutyl borate to remove some unchanged alcohol. A 65% yield of (+)-3-methyl-β-citronellal (V) was isolated.

Experimental

Elemental analyses were determined by the Schwarzkoff Microanalytical Laboratory, Woodside 77, New York.

Gas Chromatography.—Six-foot copper tubes (0.25 in. o.d.) packed with sucrose acetate isobutyrate[9a] (SAIB; 20% by wt.) deposited on 60/80 mesh Chromosorb[9b] or Hyprose SP-80[9c] (20% by wt.) on Chromosorb were used as analytical columns. Detection was carried out on an Aerograph Model A-90[9d] equipped with a thermal conductivity cell and a speedomax Model G recorder.[9e]

(+)-**Pulegone (II).**—The fractional distillation of European Oil of Pennyroyal[10] afforded (+)-pulegone of b.p. 81° (5.0 mm.), $n^{25}\text{D}$ 1.4861, $\lambda_{\text{max}}^{\text{EtOH}}$ 253 mμ, log ε 3.84, $[\alpha]^{22}\text{D}$ +23.56 (neat, 1 dm.). A GLC spectrum on SAIB and Hyprose revealed only one component in both cases. A 2,4-dinitrodiphenylhydrazone had m.p. 148.7–149°. The lit.[11] reports b.p. 102–102.5° (17 mm.), $n^{24.8}\text{D}$ 1.4853, $[\alpha]^{26.5}\text{D}$ +22.47 (neat, 1 dm.). $\lambda_{\text{max}}^{\text{EtOH}}$ 252 mμ, log ε 3.85, 2,4-dinitrophenylhydrazone m.p. 148–149°.

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(2) All structural formulas used in this paper signify absolute configuration since the absolute configuration of (−)-4-methylisopulegone (III) has been established by E. J. Eisenbraun, F. Burian, J. Osiecki, and C. Djerassi, *J. Am. Chem. Soc.*, **82**, 3476 (1960).

(3) (a) J. M. Conia, *Bull. soc. chim. France*, 943 (1954); (b) J. M. Conia, French Patent 1,113,274 (March 26, 1956).

(4) It has been reported that the sodium amide-catalyzed methylation of pulegone produces the 2-methyl isomer. *Cf.* A. Haller and P. Ramart, *Compt. rend.*, **179**, 121 (1924).

(5) It is interesting to note that 25% alcoholic sodium ethoxide has been reported to isomerize an isopulegone–pulegone mixture to pure pulegone. C. Black, G. L. Buchanan, and A. W. Jarvie, *J. Chem. Soc.*, 2971 (1956).

(6) C. Djerassi, J. Osiecki, and E. J. Eisenbraun, *J. Am. Chem. Soc.*, **83**, 4433 (1961).

(7) S. Winstein and N. J. Holness, *ibid.*, **77**, 5562 (1955); D. H. R. Barton, A. das Campos-Naves, and R. C. Cookson, *J. Chem. Soc.*, 3500 (1956).

(8) V. Grignard and J. Doeuvre, *Compt. rend.*, **190**, 1164 (1930).

(9) (a) Eastman Chemical Products Inc., Kingsport, Tennessee; (b) F. & M. Scientific Corp., New Castle, Delaware; (c) The Dow Chemical Co., Midland, Michigan; (d) Wilkens Instrument and Research Inc., Walnut Creek, California; (e) Leeds & Northrup, Philadelphia, Pennsylvania.

(10) Obtained from Ungerer and Co., New York, N. Y.

(11) E. J. Eisenbraun and S. M. McElvain, *J. Am. Chem. Soc.*, **77**, 3383 (1955).

(−)-4-Methylpulegone (III).—The procedure of Conia[3a] was followed. From (+)-pulegone (154 g., 1.0 mole), methyl iodide (200 g., 1.4 moles), 1.9 *N* sodium *t*-amylate (550 ml.), and diethyl ether (750 ml.), there was obtained 120.5 g. (71.5%) of a methylisopulegone fraction of b.p. 72–74° (2.0 mm.), $n^{27}\mathrm{D}$ 1.4738–1.4741, $\lambda_{\max}^{\mathrm{EtOH}}$ 253 mμ, log ϵ 3.44. A GLC analysis on the SAIB column showed three bands, A (12.3%), B (51.4%), and C (36.3%) in order of elution.

Treatment of this material with semicarbazide reagent[12] gave a semicarbazone of m.p. 201–205°, which after one recrystallization from ethanol melted at 204–205°. The semicarbazone of (−)-4-methylisopulegone is reported[3a] to have m.p. 203–205°. The steam distillation of the semicarbazone in the presence of 5% aqueous hydrochloric acid gave (−)-4-methylisopulegone (III) of b.p. 60° (1.0 mm.), $n^{20}\mathrm{D}$ 1.4698, $[\alpha]^{23}\mathrm{D}$ −116.5°, lit.[3a] reports b.p. 86–88° (8 mm.) $n^{19}\mathrm{D}$ 1.4711, $[\alpha]^{20}$ 578 −118.88°.

The retention time of III was found to be identical with component B in the original ketone mixture.

Component C matched the retention time of (+)-pulegone. The % pulegone calculated from the ultraviolet value (log ϵ 3.44) was 37.5%. This is in excellent agreement with the 36.3% calculated from the GLC data.

Component A failed to match the retention time of isopulegone.

4-Methylisopulegol (IV).—A solution of 4-methylisopulegone (7.0 g., 0.042 mole) in diethyl ether (50 ml.) was added dropwise to a slurry of lithium aluminum hydride (4.0 g., 0.105 mole) in diethyl ether (100 ml.). After hydrolysis with 10% sodium hydroxide there was obtained 6.3 g. (88%) of 4-methylisopulegols, b.p. 58–61° (1 mm.), $n^{20}\mathrm{D}$ 1.4790, infrared spectrum, 2.96, 6.11, and 11.27 μ. A gas-liquid chromatograph on Hyprose gave two bands, 43 and 57%, in order of elution. These isomers presumably correspond to the axial (43%) and equatorial (57%) hydroxyl isomers.

Anal. Calcd. for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.39; H, 11.92.

(+)-3-Methyl-β-citronellal (V).—An 18-in. Pyrex tube (0.75 in. i.d.) was packed loosely to a depth of 12 in. with 0.25-in. o.d. Pyrex-helices. The tube was placed in a vertically mounted electric muffle furnace so that all the packed area was in the heating zone. The system was heated so that the outer surface of the glass tube was maintained at 490–500°. 4-Methylisopulegol (28 g.) in the presence of a slow stream of nitrogen was dropped onto the heated glass helices. The pale yellow pyrolysate (24.5 g., 87.5% recovery) was collected in an ice-cooled receiver. Infrared analysis of this material showed the presence of some alcohol. To remove this the mixture was treated with excess isobutyl borate and a mixture of isobutanyl alcohol, isobutyl borate, and V was distilled. The distillate was treated with 10% sodium bicarbonate and extracted with hexane. The hexane layer was dried and distilled. There was obtained 18.5 g. (65%) of (+)-3-methyl-β-citronellal, b.p. 64–66° (2 mm.), $n^{20}\mathrm{D}$ 1.4564, $[\alpha]^{22}\mathrm{D}$ +10.62° (neat. 1 dm.), infrared 3.69, 5.81, and 7.25 μ. A GLC spectrum on SAIB showed the material to be better than 98.5% pure. The literature[1] reports for the DL-isomer, b.p. 63–64° (1 mm.), d^{20}_{4} 0.8261, $n^{20}\mathrm{D}$ 1.4549.

Anal. Calcd. for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.47; H, 11.87.

Acknowledgment.—The author wishes to thank Mr. Aaron Kossoy and his associates for GLC determinations.

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[12] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," 3rd ed., J. Wiley & Sons, Inc., New York, N. Y., 1900.

Preparation of Some Bis(nitrophenyl) Ethers, Bis(aminophenyl) Ethers, and Some Derived Azo Compounds[1]

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As part of a program to prepare unusual azo compounds, we decided to investigate the chemistry of bis(2-aminophenyl) ether (III). The reaction between 2-nitrochlorobenzene and potassium 2-nitrophenoxide to produce bis(2-nitrophenyl) ether (I), a compound which may be easily reduced to the diamine, has been known for many years.[2–4] However, yields were either very low (<6%)[2,3], or the procedure unspecified[4] (23% yield).

We found that a 72% yield of I was obtained when equimolar quantities of reactants were heated at reflux overnight in dimethylformamide. Dimethylacetamide and dimethyl sulfoxide were similarly effective as reaction solvents. The use of dimethylformamide as solvent for preparing the other bis(nitrophenyl) ethers was investigated. Table I shows the results of allowing the potassium salt of the nitrophenol in the first column to react with the nitrochlorobenzene of the second column to give the bis(nitrophenyl) ether in the yield shown. The last column gives reported yields.

TABLE I

PREPARATION OF BIS(NITROPHENYL) ETHERS

Nitro-phenoxide	Nitro-chloro-benzene	Reaction time (hrs.)	Yields, %	
			Found[a]	Reported
o	*o*	18	72,[b] 33,[c] 65[d]	23[f]
p	*o*	4.5	61	30[g]
p	*p*	16	79	85[g]
m	*p*	1	73	87[h]
m	*o*	5	60	..
m	*m*	18	0[e]	23[i]

[a] After one recrystallization. [b] Dimethylformamide. [c] Dimethyl sulfoxide. [d] Dimethylacetamide. [e] A reduction product, 3,3′-dichloroazobenzene, was isolated. [f] See ref. 4. [g] M. J. Rarick, R. Q. Brewster, and F. B. Dains, *J. Am. Chem. Soc.*, **55**, 1289 (1933). [h] R. Q. Brewster and F. Strain, *Ibid.*, **56**, 117 (1934). [i] M. Julia and G. Tchernoff, *Bull. soc. chim.* (*France*), 546 (1952).

When potassium 3-nitrophenoxide was allowed to react with 3-nitrochlorobenzene, none of the dinitrodiphenyl ether was obtained. A small quantity of an orange material was isolated which proved to

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(1) Presented in part at the Metropolitan Regional Meeting, New York and North Jersey Section, American Chemical Society, New York, N. Y., January 22, 1962.

(2) C. Haeussermann and E. Bauer, *Ber.*, **29**, 2083 (1896).

(3) N. M. Cullinane, H. G. Davey, and H. J. H. Padfield, *J. Chem. Soc.*, 719 (1934).

(4) N. L. Allinger and G. A. Youngdale, *J. Am. Chem. Soc.*, **84**, 1020 (1962).